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Ultracold Chemistry

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Chemists usually study reactions at temperatures of tens or hundreds of degrees Kelvin. Under these conditions, reaction rates are averaged over many different energies and initial conditions for collisions. But new techniques are now making it possible to produce molecules and trap them at temperatures within one millionth of a degree of absolute zero. Under these conditions, all the thermal averaging is removed: the molecules occupy the lowest possible quantum translational states and all their motions are completely controllable. On page 853 of this issue, Ospelkaus *et al.* (1) describe the very first experiments on chemical reactions between molecules in this new regime. They find that tiny and apparently insignificant changes, such as flipping the orientation of a single nuclear spin, can have profound consequences for how (and whether) chemical reactions occur.

It has been possible to cool atomic gases and trap them at sub-millikelvin temperatures for almost 25 years. Nobel Prizes were awarded for laser cooling of atoms in 1997 (2) and Bose-Einstein condensation in 2001 (3). However, it has only recently become possible to produce *molecules* in this “ultracold” regime. A major breakthrough came in 2003, when several groups (4–7) succeeded in producing molecules in atomic gases by *magnetoassociation*, in which pairs of atoms are coherently converted into molecules by carefully controlled magnetic field ramps. However, magnetoassociation produces molecules in states that are extremely weakly bound, by only about 1 part in 10^8 of normal chemical bond energies. It was only in 2008 that coherent laser techniques were developed to transfer these ultracold molecules to deeply bound states that can be regarded as chemically bonded. So far this has been achieved for only three species: KRb in Colorado (8), and Cs₂ (9) and triplet Rb₂ (10) in Innsbruck.

In the work described in this issue, pairs of ultracold KRb molecules collide and exchange atoms to form K₂ + Rb₂. The particular isotopes used here (⁴⁰K and ⁸⁷Rb) form KRb molecules that are *fermions*, with half-integer total spin. Because of the Pauli Principle, two identical fermions avoid one another quantum-mechanically through an effect called a *Fermi hole*. This greatly reduces the collision rate at low temperature, and the KRb molecules can survive for several seconds as long as they are all in the same internal quantum state. However, if some of

the molecules are converted into a different internal state by flipping the orientation of one of the nuclear spins, collisions are no longer suppressed by fermion symmetry and the molecules react 10 to 100 times faster.

Ultracold molecules have many potential applications. Dipolar molecules are expected to form a wide variety of new quantum phases (11). They may one day be used as qubits in quantum computers (12), or to probe fundamental physical symmetries through measurements of the electric dipole of the electron (13). For these applications, chemical reactions provide a trap loss mechanism that must be avoided. Fortunately, there are several routes by which this may be achieved. There are some alkali metal pairs, such as RbCs, for which atom exchange reactions are energetically forbidden, and even where reactions are allowed they may be prevented by placing the molecules in an optical lattice (9) or by creating repulsive interactions between molecules with electric fields (14).

Ospelkaus *et al.* (1) have also studied the reactions of KRb with ultracold K and Rb atoms. With K atoms, there is a fast reaction to form $K_2 + Rb$, which releases kinetic energy and ejects the products from the trap. With Rb, however, the reaction to form $Rb_2 + K$ is energetically forbidden. Provided both the Rb atoms and the KRb molecules are in their absolute ground states, the molecules are long-lived. However, if either the atoms or the molecules are placed in a different nuclear spin state, fast loss is again observed. This is something of a puzzle, as there is still no chemical pathway available and collisions that change *only* the orientation of a nuclear spin should be suppressed by centrifugal barriers at these temperatures.

Magnetoassociation is not the only approach being used to form ultracold molecules. Other groups have produced deeply bound ultracold molecules from atoms by *photoassociation*, in which laser light is used to transfer pairs of atoms directly into molecular states by spectroscopic transitions (15). However, so far the yields of ground-state molecules in such experiments have been relatively low and quantum-mechanical coherence has not been achieved.

Both magnetoassociation and photoassociation are limited to molecules formed from atoms that can themselves be laser-cooled. In practice this limits them to molecules formed from alkali metals, alkaline earths, and a very few other atoms. Such molecules have a quite limited chemistry, so there is an intense parallel effort to cool preexisting molecules to the ultracold regime, using techniques such as buffer-gas cooling in cryogenic helium (16) and deceleration of molecular beams with switched electric and magnetic fields (17). These methods can be applied to a much wider range of molecules, including chemically important polar molecules such as ammonia and free radicals such as OH and NH. So far these “direct cooling” methods have only achieved temperatures of 10 to 100 millikelvin, which is not quite in the ultracold regime. Nevertheless, it is highly likely that ways will soon be found to cool these species too to sub-millikelvin temperatures, paving the way for a new type of quantum-controlled ultracold chemistry.

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Fig. 1. Two KRb molecules at temperatures below 1 microkelvin can react to form $K_2 + Rb_2$, but the rate is suppressed by fermion symmetry when the two molecules are in identical quantum states.